

## Stable Isotopes of Water in Hydrogeology

S. Tweed<sup>1</sup>, Marc Leblanc<sup>2</sup>, I. Cartwright<sup>3</sup>, A. Bass<sup>4</sup>, Y. Travi<sup>2</sup>, V. Marc<sup>2</sup>, T. Nguyen Bach<sup>5</sup>, N. Dang Duc<sup>6</sup>, S. Massuel<sup>1</sup>, and U. Saravana Kumar<sup>7</sup>

<sup>1</sup>UMR G-eau, IRD, Montpellier, France

<sup>2</sup>University of Avignon, Avignon, France

<sup>3</sup>Monash University, Clayton, Victoria, Australia

<sup>4</sup>University of Glasgow, Glasgow, UK

<sup>5</sup>Hanoi University of Mining and Geology, Hanoi, Vietnam

<sup>6</sup>Institute for Nuclear Sciences and Technologies, Hanoi, Vietnam

<sup>7</sup>Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

### 1 Introduction

Managing water resources requires a comprehensive understanding of the interactions between the various water cycle components, and the study of dynamic water systems requires approaches capable of capturing processes across multiple spatial and temporal scales. Globally, there are monitoring networks of water resources, mostly focused on physical parameters. However, the spatial and temporal resolution of both surface water and groundwater data often remains insufficient to capture the full variability of these hydrosystems. Because groundwater systems respond slowly to change, using only physical parameters also does not enable the determination of changes in flow pathways, such as the mixing between different systems, or interactions between groundwater and surface water. Approaches to compensate for the incomplete physical monitoring data have included the incorporation of numerical modeling [1], remote sensing [2], and environmental tracers (ubiquitous natural or anthropogenic compounds found in the Earth's surface and subsurface [3]).

As presented in this article, the stable isotopes of waters are a well-established environmental tracer. Here, we review the use of stable oxygen and hydrogen isotopes to understand the origin, pathways, and chemical evolution of groundwater (Figure 1). This article provides an overview of the use of stable isotopes to analyze (i) groundwater recharge from both rainfall and irrigation water, and presents case studies that highlight the use of stable isotopes to determine the frequency, rapidity, and origins of

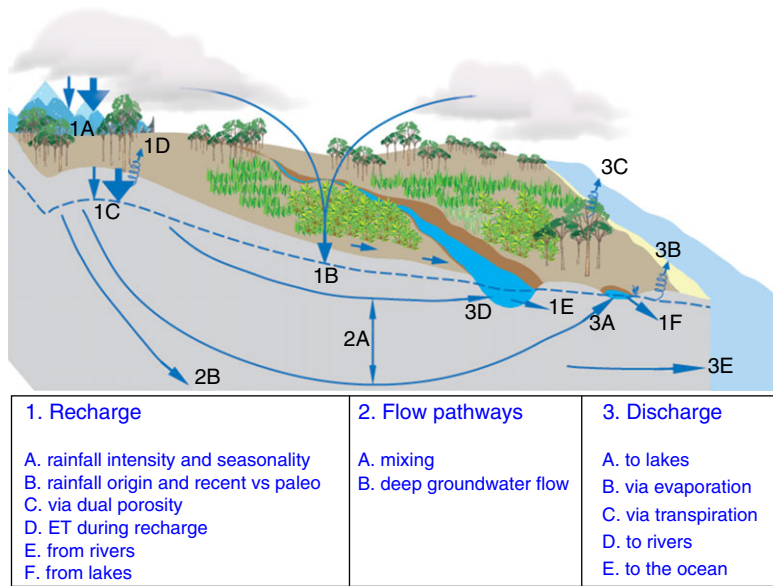
recharge; (ii) groundwater flow pathways including paleo-groundwater and mixing processes, and case studies of deeply circulating mineral waters, groundwater mixing, and origins of paleo-groundwater; (iii) groundwater discharge via evaporation, surface waters, and case studies that highlight the modeling of dynamic tropical river inflows and submarine groundwater discharge; and (iv) groundwater salinity, including a comparison of processes driving salinization in two regional groundwater basins.

### 2 Summary of Stable Isotopes of Water

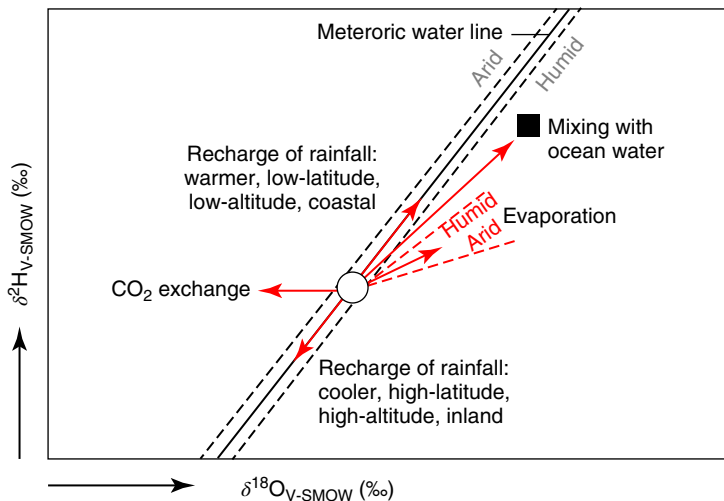
Isotopes of a given element have the same number of protons but differ in the number of neutrons and therefore atomic mass. Unlike the radiogenic isotopes, the stable isotopes do not decay over geological timeframes. The stable isotopes of oxygen and hydrogen in waters are <sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O and <sup>1</sup>H and <sup>2</sup>H, respectively. Stable isotope ratios are expressed as  $\delta$  values, for example  $\delta^{18}\text{O}$  is defined as:

$$\delta^{18}\text{O} = \frac{\left(\frac{{}^{18}\text{O}}{{}^{16}\text{O}}\right)_{\text{Sample}} - \left(\frac{{}^{18}\text{O}}{{}^{16}\text{O}}\right)_{\text{Std}}}{\left(\frac{{}^{18}\text{O}}{{}^{16}\text{O}}\right)_{\text{Std}}} \times 1000 \quad (1)$$

$\delta^{18}\text{O}$  is the difference in the <sup>18</sup>O/<sup>16</sup>O ratio between the sample and standard ( $S_{\text{td}}$ ) in per mil (‰). Vienna-Standard Mean Oceanic Water (V-SMOW), which has the average <sup>18</sup>O/<sup>16</sup>O and <sup>2</sup>H/<sup>1</sup>H of the oceans, is used as the standard for water analyses. Isotope ratios change (fractionate) due to the mass differences, which for <sup>18</sup>O/<sup>16</sup>O is 12.5% and for <sup>2</sup>H/<sup>1</sup>H is 100%. This may occur during a phase change (e.g. evaporation of



**Figure 1** Summary of the hydrogeological processes investigated using stable isotopes of waters.



**Figure 2** Processes discussed in this article that are analysed using stable isotopes of waters.

liquid water into water vapor) or isotopic exchange between two phases (water/gas or water/solid). At a given temperature and humidity, isotope fractionation occurs predictably and therefore provides information on hydrological processes, including evaporation and rainfall [4] (Figure 2). In particular, the fractionation of  $^{18}\text{O}$  and  $^2\text{H}$  in groundwater can act as a fingerprint of origin (Section 3) and, often associated with groundwater chemistry, provides insights in salinization processes (Section 6). Stable isotope ratios of rainfall and surface water may be variable due to fractionations that occur in individual storm events controlled by temperature, the origin of the moisture, and rainfall generation. However, the stable isotope ratios of groundwater are generally more homogeneous due to mixing within aquifers. This can attenuate

both event-scale variation and longer-term climate variations.

Stable isotopes of water are one of the many environmental tracers used to study water cycle processes and are present in the atmosphere, biosphere, lithosphere, and the hydrosphere. The main advantage of using  $^{18}\text{O}$  and  $^2\text{H}$  over other environmental tracers (e.g.  $^{13}\text{C}$ ,  $^{14}\text{C}$ ,  $^{222}\text{Rn}$ ,  $^3\text{H}$ ,  $\text{SF}_6$ , CFCs and major, minor or trace ions) is that they are part of the water molecule. In addition, recent technological developments in laser spectrometry now allow continuous, *in situ*  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  measurements at a very fine temporal resolution (e.g. 30 s [5]); therefore, offering the possibility of capturing the variability in real time of rapid hydrosystem processes.

### 3 Recharge

#### 3.1 Rainfall Recharge

The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of rainfall vary in time and space owing to the dependence of temperature on isotopic fractionation. Accordingly, spatial variations may occur when air masses loaded with marine vapors gradually become poorer in heavy isotopes as they progress inland and the cloud becomes higher [4]. This situation implies for each region the definition of a meteoric water line at the local scale (local meteoric water line (LMWL)), which has been made easier by the global database of rainfall isotope values [6]. At smaller scales, this variation can also be the consequence of isotopic depletion with altitude (altitudinal effect [7]). This last property is commonly used to estimate the altitude of groundwater recharge for springs or pumping wells in mountain areas [8–10]. At any locality, there is also a wide variation over time in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of rainfall. At the seasonal scale, a cyclical evolution (isotopic depletion in winter, enrichment in summer) of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in rainwater is commonly observed according to the changes in the atmospheric temperature. At a given point, the analysis of the relative attenuation of the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values in rainwater and groundwater can provide information on the efficiency and velocity of water transfers [11, 12].

#### 3.2 Excess Irrigation

In Mediterranean and semi-arid climate regions, irrigation is commonly used not only for the agricultural development of the territories but also for the recharge of shallow groundwater. The impact of irrigation on recharge depends largely on the method of irrigation. For example, gravity-fed irrigation greatly enhances the recharge of the underlying water table [13, 14].

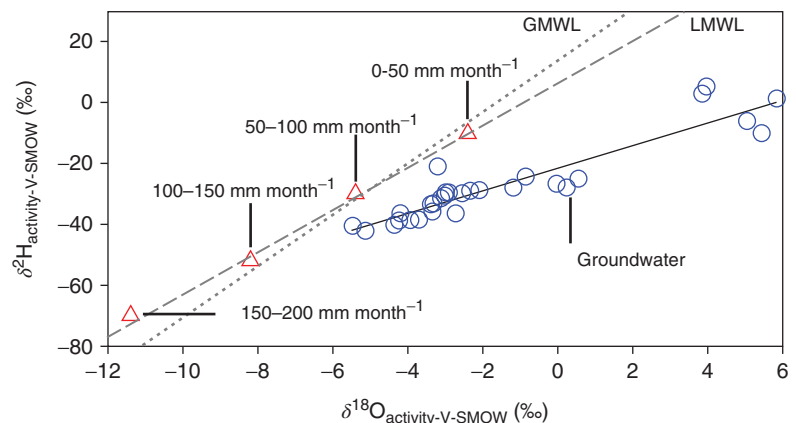
This immersion irrigation is only possible in the case of a large water availability linked to the proximity of large hydrographic systems. In the south-east of France, the Rhone and Durance basins have enabled the development of a dense network of channels dedicated to gravity irrigation. The effect of this irrigation on recharge is generally difficult to quantify because the spatial and temporal variability of water volumes is often poorly understood. Isotopic tracing is an efficient alternative because these waters, of alpine origin, have lower  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values compared to local rains [15, 16]. This configuration or any other local situation discriminating the water bodies involved produces mixing maps showing the spatial variability of irrigation recharge [17, 18]. If the surface waters also show a marked seasonal isotopic variability, for example due to the alternation of their snowy or rainy origins, this can be used through isotopic transfer models to extract information on water residence times in the aquifer system [19, 20].

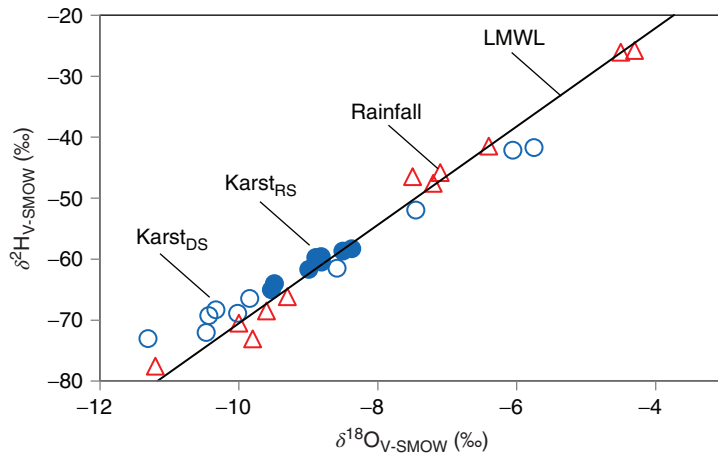
#### 3.3 Case Studies

##### 3.3.1 Recharge from Sporadic Heavy Rain

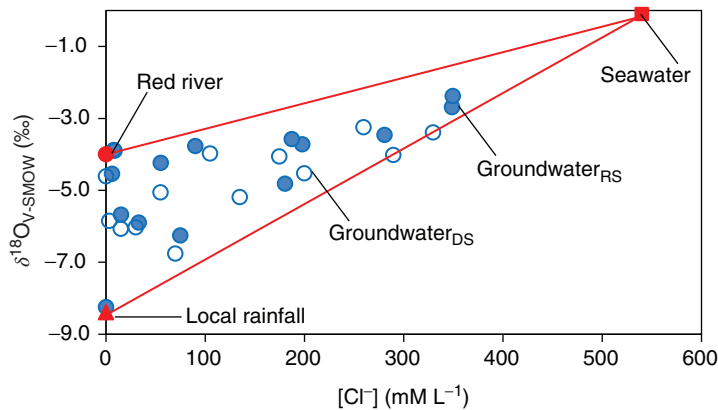
A study in the Lake Eyre Basin (LEB), located in arid central Australia, used the rainout effect on stable isotope values to indicate the size of rainfall events predominantly recharging the groundwater system [21]. The linearly interpolated isotope values for groundwater were estimated at  $\sim -9$  and  $-57\text{‰}$  for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , respectively. At these values, the corresponding local rainfall levels are  $>100\text{--}150\text{ mm month}^{-1}$  (data after [22]; Figure 3). The spatial average of the long-term gridded rainfall data (1900–2006) shows that the highest average monthly rainfall level is  $33\text{ mm}$  during January. Therefore, groundwater recharge is predominantly from sporadic heavy storms, which are not a regular occurrence.

**Figure 3**  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  activities for groundwater located in arid central Australia (Lake Eyre Basin) compared with the global meteoric water line (GMWL; [23]) and local MWL (LMWL, Alice Springs station, IAEA/WMO, 2006). Also presented are the weighted mean isotopic compositions of rainfall events ranging from  $0\text{--}50\text{ mm month}^{-1}$  to  $>200\text{ mm month}^{-1}$ . Source: Tweed et al. [21]. Reproduced with permission of Elsevier.





**Figure 4** The local meteoric water (LMWL) and water sampled from resurgences and springs in the karstic area of NE Vietnam (Thai Nguyen, Tuyen Quang, Bac Kan, Ha Giang, Lang Son and Quang Ninh provinces) in dry ( $\text{Karst}_{\text{DS}}$ ) and rainy ( $\text{Karst}_{\text{RS}}$ ) seasons. Source: Dang Duc et al. [24]. Reproduced with permission of Springer Nature.



**Figure 5** The  $\delta^{18}\text{O}$  vs  $[\text{Cl}^-]$  relationship for groundwater during the dry (DS) and rainy (RS) season in the Holocene aquifer, Red River delta plain (Vietnam). The groundwater stable isotope values represent variations in recharge from the three sources: local rainfall, Red River water and seawater. Source: Hoang et al. [25]. Reproduced with permission of Springer Nature.

### 3.3.2 Rapid Rainfall Recharge

Springs and resurgences in the karstic region of the northeast provinces of Vietnam (Thai Nguyen, Tuyen Quang, Bac Kan, Ha Giang, Lang Son, and Quang Ninh with an area of 38 921 km<sup>2</sup>) have  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values close to that of local rainfall (Figure 4). These stable isotope values plus the high tritium values of the springs reflect rapid local recharge. This was attributed to the concentrated autogenic rainwater runoff funneled into sinkhole depressions, which drain rapidly to the subsurface through swallets [24].

### 3.3.3 Mixed Origins of Recharge

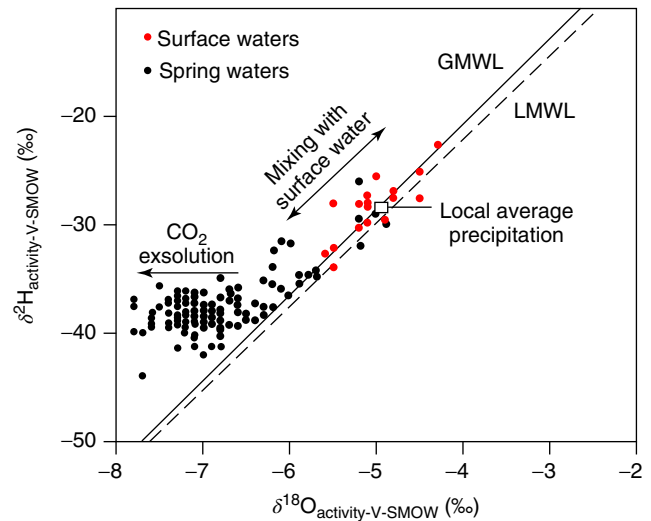
Groundwater recharge to the shallow Holocene aquifer in the southern-most part of the Red River delta plain, Nam Dinh province (Vietnam), was identified as a mix from three sources: (i) the local precipitation through vertical infiltration, (ii) from the Red River and (iii) from the Southeast Sea (former South China Sea). The contribution of each source contributing to groundwater recharge was estimated based on  $\delta^{18}\text{O}$  values and chloride concentrations in each individual water type (Figure 5 [25]).

## 4 Groundwater Flow Pathways

### 4.1 Paleo-Groundwater and Mixing

Groundwater is a valuable archive of past climates. Groundwater in large basins commonly has residence times of several thousands to hundreds of thousands of years and thus preserves a record of changes to the hydrosphere that extends into Pleistocene [26–28]. Combining residence time estimates with geochemical studies potentially allows the changing conditions in the groundwater recharge area to be determined. Globally, the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of rainfall correlate both spatially and temporally with global temperatures, and the  $\delta^{18}\text{O}$  values of rainfall during the last glacial maximum were several permil lower than those of present-day rainfall [29, 30]. Large aquifer systems at higher latitudes throughout Europe, Asia, and North America commonly preserve low  $\delta^{18}\text{O}$  groundwater recharged during the retreat of the ice sheets [27, 31, 32]. In addition, changes to global rainfall patterns resulting from changing climate conditions may be reflected in groundwater. For

**Figure 6**  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of spring waters and surface water, located in south eastern Australia, relative to the global (GMWL) and local (LMWL) meteoric water lines. The trend in  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  values of the spring waters is due to  $\text{CO}_2$  exsolution at low temperatures, while the spread of mineral spring waters to higher  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values reflects mixing with younger shallower groundwater or surface water in the discharge areas. Source: Cartwright et al. [35]. Reproduced with permission of Elsevier.



example, low  $\delta^{18}\text{O}$  groundwater from north-central China reflects periods of increased recharge from the East Asian Monsoon that commonly reached this region prior to  $\sim 10$  ka [33, 34]. Similar monsoonal recharge is recorded in African groundwater and preserves a record of alternating pluvial and arid periods [31]. Aside from providing valuable evidence of changes to the climate system over the last few tens-of-thousands of years, identification of palaeowaters is vital for assessing the sustainability of water use. In water-limited areas, such as parts of northern China and Africa, the palaeowaters represent a finite source of useable water that is not necessarily being replenished under current climatic conditions [31, 34]. In addition, the distinctive stable isotope compositions of these waters allow mixing between aquifers to be detected, which is invaluable in understanding both natural and anthropogenically impacted groundwater flow.

## 4.2 Case Studies

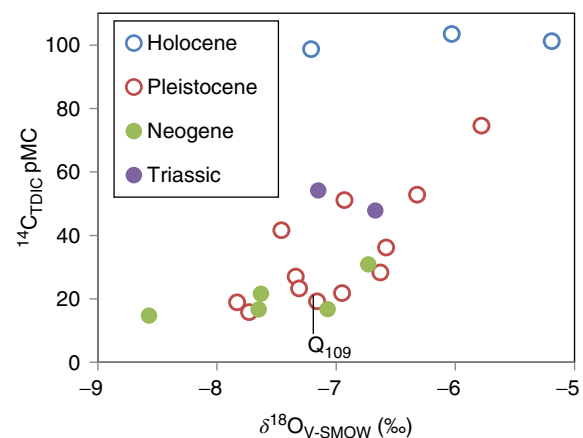
### 4.2.1 Deeply Circulating Groundwater

The  $\delta^2\text{H}$  values of the spring waters ( $-45$  and  $-35\text{‰}$ ) in temperate south eastern Australia are lower than modern rainfall values (weighted average  $-29\text{‰}$ ; IAEA data 1969–1991) (Figure 6 [35]). Using the relationship between mean annual air temperature (MAAT) and  $\delta^2\text{H}$  values [36] this suggests recharge temperatures of  $9.6$  to  $11.6\text{ °C}$  for the  $\delta^2\text{H}$  values of the spring waters. This is below the present-day MAAT for the study region ( $13.0$ – $14.0\text{ °C}$ ) and suggests that the springs were recharged under colder climatic conditions ( $\sim 3.5$ – $3.0$  ka BP). In addition, the  $\delta^{18}\text{O}$  values of the spring waters in the fractured basalt aquifer show that as the deeply circulating waters are transported to the surface the  $\text{CO}_2$  exsolves, and exsolution of  $\text{CO}_2$  lowers the  $\delta^{18}\text{O}$  values

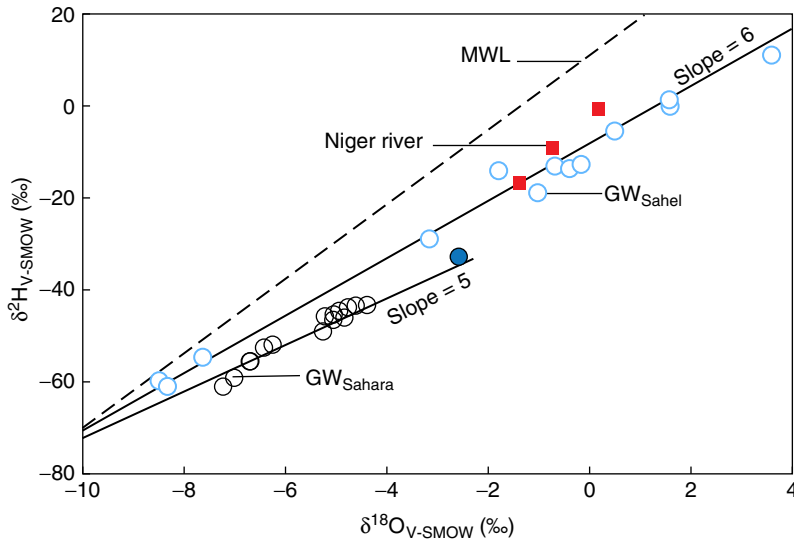
of the water, driving values to the left of the LMWL and global meteoric water line (GMWL) (Figure 6).

### 4.2.2 Pumping Induced Mixing

Stable isotopes of groundwater within the deep aquifers of the southern Red River delta plain (Nam Dinh province, Vietnam) highlight areas where groundwater abstraction causes inter-aquifer mixing [25]. The groundwater abstraction rate of  $95\,000\text{ m}^3\text{ day}^{-1}$  from the Q109 borehole exceeded the recharge rate and induced inter-aquifer leakage. This was evident from the  $^{14}\text{C}$  and  $\delta^{18}\text{O}$  values of groundwater from this Pleistocene aquifer (e.g. Q109; Figure 7); which did not significantly differ from  $\delta^{18}\text{O}$  of groundwater from the underlying Neogene aquifer.



**Figure 7** The  $^{14}\text{C}$  and  $\delta^{18}\text{O}$  (dry season) values for groundwater from the southern Red River Delta aquifers in the Nam Dinh province (Vietnam). The aquifers in order from shallowest to deepest are: Holocene, Pleistocene, Neogene and Triassic. Source: Hoang et al. [25]. Reproduced with permission of Springer Nature.



**Figure 8** Stable isotopes from the Niger River area in northern Mali, where evaporated signatures (slopes 5 and 6) distinguish groundwaters from the Sahara ( $GW_{Sahara}$ ; north of the Azaouad ridge) to those in the Sahel ( $GW_{Sahel}$ ; Nara Trench, Timbuktu and south of Azaouad ridge). Sahel groundwater are located to the south and originate from Niger River recharge. Source: Fontes et al. [37]. Reproduced with permission of John Wiley & Sons.

#### 4.2.3 Origin of Paleo-Groundwater

The area north of the Niger River, northern Mali including the Azaouad depression, has been recharged during past river flooding episodes as well as directly from rain during Holocene wet periods. Historically, the Niger River has migrated from north to south across the Nara trench over a period of about 4000 years since the end of the Holocene wet period. The chemical and isotopic signature of the groundwater north of the Azaouad ridge (Sahara) suggests groundwater originates from rain during the Holocene wet periods (Figure 8). This groundwater from the Sahara has a distinct slope of the evaporation line compared with groundwater sampled in the south (Sahel) that originates from Niger River recharge [37].

## 5 Discharge

### 5.1 Salt Pans and Evaporation

$\delta^{18}O$  and  $\delta^2H$  data indicate whether shallow groundwater has been significantly evaporated since this causes fractionation to the right of the meteoric water line (Figure 2). Evaporated water from open pans defines evaporation trends with slopes of 3.9 at 0% humidity and close to 8 as humidity approaches 100% [38]. Evaporation trends with slopes of  $<3.9$  can be attributed to salinity effects. At high salinities, there is decreased fractionation, and reversals in fractionation can occur due to the reduced humidity contrast between the boundary layer and open atmosphere from decreased activity of water [4]. However, this would result in a low slope only for the more saline groundwater samples. Experimental stable isotope work suggests that arid zone water evaporated through dry soil can also result in a lower

slope, compared with evaporation that predominantly occurs from surface water or the water table (slope is typically 4–6 [39, 40]). Mathematical modeling indicates that under dry conditions evaporation of water results in a slope that is 30% less than evaporation from wet soils under the same conditions [40]. In the arid Lake Eyre, the slope of 2.97 for regional groundwater is 27% less than the slope of 4.05 for groundwater sampled from the shallow water table ( $<2$  m depth from surface) under the Lake Eyre bed and shoreline, where evaporation occurs under more humid conditions [21].

### 5.2 Groundwater Discharge to Surface Water

Stable isotopes are also commonly used to determine groundwater and surface water interactions since in comparison with other methods (e.g. hydraulics and seepage meters), they can integrate processes over a range of spatial and temporal scales [41–45]. In combination with other tracers (typically major ion concentrations, electrical conductivity or radioactive isotopes), the variation of stable isotope ratios allow the changing water sources at different stages of lake levels or river flow to be determined. For example, over flood hydrographs (i.e. those that occur following heavy rainfall events), these studies commonly illustrate that much of the water that discharges to the stream is from stores within the catchment rather than being recent rainfall (commonly termed the “old water paradox” [46]). Specifically, many studies have used isotopic methods to distinguish event versus pre-event waters contributing to river flow [47–50], to identify inflows to rivers from different provinces at the regional scale [51], and to quantify mean transit time and mixing proportions between stream water and groundwater

[52, 53]. Stable isotopes are also used to investigate the groundwater interactions with lakes [54], and ocean water [55].

Although there has been much research in using stable isotopes to study groundwater and river interactions, several uncertainties and questions remain. Primarily, most hydrograph separations are made assuming two components (the new or storm-water input and a baseflow component from within the catchment). However, detailed geochemistry studies commonly show that there may be multiple sources of water (e.g. groundwater, interflow, soil water, and surface water) that contribute to streamflow during different flows [42, 44, 56]. In addition, estimating the proportion of water derived from the different stores requires that the stable isotope ratios of those waters are relatively constant. While that may be the case for groundwater, water from the unsaturated zone or soils may have more variable  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values that introduce uncertainties into the calculations [44]. In a similar way, the stable isotope ratios of rainfall may also be variable. In many studies, the rainfall input is represented by a single sample; while the stable isotope ratios of rainfall are likely to be both spatially and temporally variable [45]. For these reasons, determining the detailed variation of stable isotopes and other tracers in streams over the course of a flow event is becoming more common, and informs our understanding of changing water stores [57, 58].

### 5.3 Case Studies

#### 5.3.1 Groundwater Discharge to a Tropical Stream

Measuring and modeling tropical fluvial systems is complicated by the localized and sporadic nature of rainfall, often coupled with rapid and substantial fluvial responses. To capture rapid tropical hydrological processes, in Scheu Creek (a perennial stream in the wet-tropical region of northeast Australia) a Wavelength

Scanned-Cavity Ring-down Spectrometer (Picarro L2120) fitted with a diffusion sampler (DS-CRDS [5]) was used to measure stable isotope values of river water at one-minute intervals [57]. The high-resolution river  $\delta^{18}\text{O}$  data was analyzed using a two-component mixing model [4, 12]:

$$Q_e = Q_c \frac{\delta^{18}\text{O}_c - \delta^{18}\text{O}_{pe}}{\delta^{18}\text{O}_e - \delta^{18}\text{O}_{pe}} \quad (2)$$

In Eq. (2), the event water input to the stream ( $Q_e$ ) is calculated using the discharge values of stream ( $Q_c$ ), and  $\delta^{18}\text{O}$  values of the stream ( $\delta^{18}\text{O}_c$ ), pre-event ( $\delta^{18}\text{O}_{pe}$ ), and event waters ( $\delta^{18}\text{O}_e$ ). The weighted average of rainfall measurements was used for the event water value and the average of the groundwater samples was used for the pre-event water value. The model results revealed that prior to and during the first six hours of the storm the stream was sustained by pre-event water inflows (unsaturated or saturated zone sources), followed by event water inflow (direct rainfall recharge, overland flow, or recently recharge subsurface inflows).

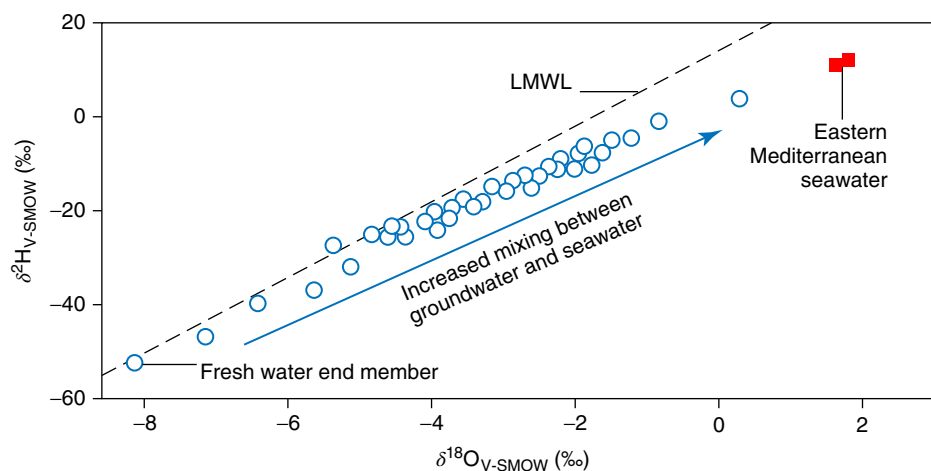
#### 5.3.2 Groundwater Interaction with Seawater

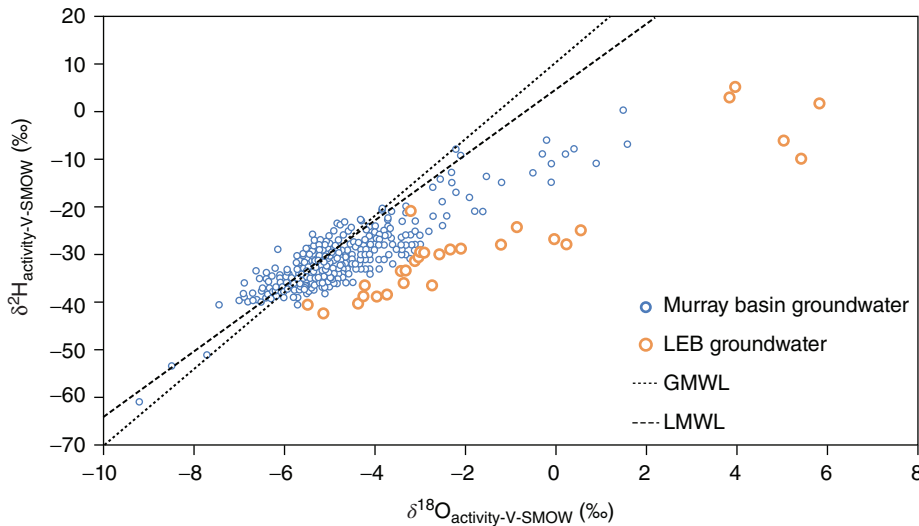
In southern Turkey, stable isotopes were used to highlight the groundwater submarine discharge and interactions with the seawater [59]. Fresh groundwater from the coastal karstic aquifer has lower  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values than those of eastern Mediterranean seawater. The stable isotope values highlight a large variation in the degree of mixing between groundwater and seawater (Figure 9).

## 6 Groundwater Salinity

Processes found to have resulted in high levels of groundwater salinity include evaporation [60], transpiration

**Figure 9** Stable isotope values of submarine groundwater discharging from a coastal karstic aquifer in southern Turkey, the local MWL and eastern Mediterranean seawater values. Source: Bayari et al. [59]. Reproduced with permission of Springer Nature.





**Figure 10**  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  activities for groundwater from the Lake Eyre Basin (LEB) and the Murray Basin groundwater located in central and eastern Australia, compared with the global meteoric water line (GMWL; [23]) and local MWL (LMWL, Alice Springs station, IAEA/WMO, 2006). Source: From [21, 66].

[61], and mixing processes such as seawater intrusion [62], and recycling of evaporites [63]. Stable isotopes of waters are particularly useful in distinguishing the evaporation from the transpiration effects on increases in groundwater salinity since the process of evaporation results in a fractionation of the stable isotopes from the meteoric water lines whereas transpiration does not [61, 64, 65]. Stable isotopes of waters have also been used to delineate the migration of saline waters throughout a groundwater basin [66]. Many arid zone studies have shown that stable isotope values can reflect the mixing between a primary brine formed by evaporation (enriched stable isotope values), and a secondary brine formed by dissolution of halite during infiltration of rainfall (depleted stable isotope values) [67, 68].

## 6.1 Case Study

### 6.1.1 Evaporation Versus Transpiration

Salinity processes in two regional systems in central and eastern Australia are presented; the LEB [21] and the Murray Groundwater Basin (MGB [66]). For the LEB Basin, a ca. 1.14 M km<sup>2</sup> endorheic basin, the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  data indicate that groundwater in the shallow aquifer has been evaporated (Figure 10). The slope of the least squares fit linear trendlines for all unconfined groundwater (3.85) samples highlight fractionation from the GMWL and LMWL. The enrichment of stable isotope values for groundwater from the estimated rainfall values are high (4–15‰ for  $\delta^{18}\text{O}$  activity, and 16–63‰ for  $\delta^2\text{H}$  activity), which reflects the extreme arid conditions and an evaporation control, rather than transpiration, on groundwater salinization.

In comparison, in the MGB (ca. 300 000 km<sup>2</sup>) the concentration of cyclic salts over tens of thousands of years in the unsaturated and saturated zones via transpiration is one of the dominant processes controlling the high salinity values of groundwater [61, 66]. This is reflected in many of the MGB samples that show little displacement of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values from the MWLs (Figure 10). Remnant vegetation in this basin is dominated by species efficient in transpiration, especially the native eucalyptus trees. However, since European settlement in the early 1800s, much of the land was cleared for new farming areas, which has decreased transpiration and resulted in an increase in groundwater recharge [69]. Therefore, many groundwater  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values in the MGB still largely reflect pre-land clearing conditions, and the full effects of land cover change on groundwater chemistry in this basin are potentially yet to be fully realized.

## 7 Directions for Future Research

### 7.1 Technological Development

The recent advancements in the high temporal resolution field measurements of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  have become essential in exposing rapid hydro(geo)logical change. For example, in small tropical sub-catchments, the synchronous measurement of river flow and  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values allows us to examine the changing stores of water over hydrographs. Further work in the application of high temporal resolution  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  measurements will help to further elucidate the dynamic evolutions of groundwater recharge, flow pathway, and discharge processes during intense rainfall events.



## 7.2 Global Changes Studies

At larger spatiotemporal scales, the evolution of the chemical system can be relatively delayed compared to the physical system. For example, at the basin scale, the study of deforestation impacts in the MGB highlighted major differences between the response of the physical system (rising groundwater levels as a result of deforestation) and the stable isotopes of groundwater (that represent salinity processes pre-dating deforestation). Therefore, in relatively large or slowly evolving hydrogeological systems the differences between the physical system and the stable isotope values of groundwater may limit the use of these as tracers of present-day climate or land cover change impacts. However, the difference in these responses can also be advantageous because the stable isotopes of groundwater can highlight the dominant historical processes that the current physical system may no longer represent. This has long been used as an approach in paleohydrogeology. However, since stable isotopes can characterize a groundwater system predating anthropogenic practices and present-day climate variability, future applications of stable isotopes can also help us to improve our understanding of the

propagation of more recent global change impacts on groundwater within a basin.

## 7.3 Global Network and Science Outreach

An essential part of analyzing groundwater stable isotope values is the comparison with rainfall and surface water values. This has been made easier and affordable through the global IAEA (International Atomic Energy Agency) data acquisition network for rain (Global Network of Isotopes in Precipitation; GNIP) and rivers (Global Network of Isotopes in Rivers; GNIR). This stable isotopes data provide historical and recent time-series for selected sites around the world. Since stable isotopes of water will continue to play a key role in groundwater resources studies, there is also a future interest to develop a Global Network of Isotopes in Groundwater (GNIG). In addition to expanding data networks, it is essential that the IAEA continues to provide training in the use of stable isotopes in hydrogeology via research (e.g. IAEA Coordinated Research Projects) and conference (e.g. IAEA International Symposium on Isotope Hydrology) platforms.

## References

- Crosbie, R.S., Pickett, T., Mpelasoka, F.S. et al. (2013). *Clim. Chang.* 117 (1–2): 41–53.
- Leblanc, M.J., Tregoning, P., Ramillien, G. et al. (2009). *Water Resour. Res.* 45: W04408.
- Baudron, P., Barbecot, F., Aróstegui, J.L.G. et al. (2013). *Hydrol. Process.* doi: 10.1002/hyp.9771.
- Clark, I.D. and Fritz, P. (1997). *Environmental Isotopes in Hydrogeology*. CRC Press.
- Munksgaard, N.C., Wurster, C.M., and Bird, M.I. (2011). *Rapid Commun. Mass Spectrom.* 25: 3706–3712.
- Schotterer, U., Oldfield, F., and Froehlich, K. (1996). *GNIP. Global Network for Isotopes in Precipitation*, 47 pp. Bern (Switzerland): Laederach AG. ISBN: 3-9521078-0-8.
- Yurtsever, Y. and Gat, J.R. (1981). In: *Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle*, IAEA Tech. Rep. Ser., vol. 210 (ed. J.R. Gat and R. Gonfiantini), 103–142. IAEA.
- Guglielmi, Y., Bertrand, C., Compagnon, F. et al. (2000). *J. Hydrol.* 229: 138–148. doi: 10.1016/S0022-1694(00)00166-9.
- Gonfiantini, R., Roche, M.-A., Olivry, J.-C. et al. (2001). *Chem. Geol.* 181: 147–167.
- Marc, V., Bertrand, C., Malet, J.-P. et al. (2017). *Hydrol. Process.* 31: 364–381. doi: 10.1002/hyp.11030.
- Soulsby, C., Malcolm, R., Helliwell, R. et al. (2000). *Hydrol. Process.* 14: 747–762. doi: 10.1002/(SICI)1099-1085(200003)14:4<747::AID-HYP970>3.0.CO;2-0.
- Lee, E.S. and Krothe, N.C. (2001). *Chem. Geol.* 179 (1–4): 129–143.
- Oliosio, A., Lecerf, R., Baillieux, A. et al. (2013). *Procedia Environ. Sci.* 19: 691–700.
- Baillieux, A., Oliosio, A., Trolard, F. et al. (2015). *Géologues* 187: 85–92.
- Lacroix, M. and Blavoux, B. (1995). *Hydrogéologie* 1: 13–20.
- Nofal, S., Cognard-Plancq, A.L., Marc, V. et al. (2012). Impact de la gestion des eaux d'irrigation sur la recharge des nappes en basse Provence : exemple de la plaine d'Avignon. In *De l'eau agricole à l'eau environnementale en Méditerranée, Résistance et adaptation aux nouveaux enjeux de partage de l'eau en Méditerranée*, Coordination C. Aspe, Edition Quae, Paris, France, 159–173. ISBN 9782759216963 (384 pp).
- Harvey, F.E. and Sibray, S.S. (2001). *Groundwater* 39: 408–421.
- Qin, D., Qian, Y., Han, L. et al. (2011). *J. Hydrol.* 405: 194–208.
- Koeniger, P., Leibundgut, C., and Stichler, W. (2009). *Isot. Environ. Health Stud.* 45: 289–302.

- 20 Eberts, S.M., Böhlke, J.K., Kauffman, L.J., and Jurgens, B.C. (2012). *Hydrogeol. J.* 20: 263–282.
- 21 Tweed, S., Leblanc, M., Cartwright, I. et al. (2011). *J. Hydrol.* 408: 257–275.
- 22 Harrington, G.A., Cook, P.G., and Herczeg, A.L. (2002). *Ground Water* 40 (5): 518–528.
- 23 Craig, H. (1961). *Science* 133: 1702–1703.
- 24 Dang Duc, N., Van Nguyen, I., Ha Ch Ha, L. et al. (2011). *Environ. Earth Sci.* doi: 10.1007/s12665-011-0943-x.
- 25 Hoang, H.V., Nguyen, L.V., Dang, N.D. et al. (2018). *Environ. Earth Sci.* 77–674. doi: 10.1007/s12665-018-7857-9.
- 26 Edmunds, W.M. (2001). *Palaeowaters in European Coastal Aquifers - The Goals and Main Conclusions of the PALAEAUX Project*, 1–16. Geological Society Special Publication.
- 27 Loosli, H.H., Aeschbach-Hertig, W., Barbacot, F. et al. (2001). *Isotopic Methods and Their Hydrogeochemical Context in the Investigation of Palaeowaters*, 193–212. Geological Society Special Publication.
- 28 Jasechko, S., Perrone, D., Befus, K.M. et al. (2017). *Nat. Geosci.* 10: 425.
- 29 Petit, J.R., Jouzel, J., Raynaud, D. et al. (1999). *Nature* 399: 429–436.
- 30 Jasechko, S. (2016). *Geochem. Geophys. Geosyst.* 17: 3274–3288.
- 31 Edmunds, W.M. (2009). *Hydrol. Sci. J.* 54: 781–792.
- 32 McIntosh, J.C. and Walter, L.M. (2006). *Geochim. Cosmochim. Acta* 70: 2454–2479.
- 33 Kreuzer, A.M., von Rohden, C., Friedrich, R. et al. (2009). *Chem. Geol.* 259: 168–180.
- 34 Currell, M.J., Han, D., Chen, Z., and Cartwright, I. (2012). *Hydrol. Process.* 26: 4050–4066.
- 35 Cartwright, I., Weaver, T., Tweed, S. et al. (2002). *Chem. Geol.* 185: 71–91.
- 36 Dansgaard, W. (1964). *Tellus* 16: 436–468.
- 37 Fontes, J.-C., Andrews, J.N., Edmunds, W.M. et al. (1991). *Water Resour. Res.* 27 (2): 199–214.
- 38 Gonfiantini, R. (1986). In: *Handbook of Environmental Isotope Geochemistry, Vol. 2 The Terrestrial Environment* (ed. P. Fritz and J.C. Fontes), 113–186. Amsterdam: Elsevier.
- 39 Allison, G.B. (1982). *J. Hydrol.* 55: 163–169.
- 40 Barnes, C.J. and Allison, G.B. (1983). *J. Hydrol.* 60: 141–156.
- 41 Sklash, M.G. and Farvolden, R.N. (1979). *J. Hydrol.* 43: 45–65.
- 42 Uhlenbrook, S. and Hoeg, S. (2003). *Hydrol. Process.* 17: 431–453.
- 43 Cook, P.G. (2012). *Hydrol. Process.* doi: 10.1002/hyp.9493.
- 44 Klaus, J. and McDonnell, J.J. (2013). *J. Hydrol.* 505: 47–64.
- 45 Fischer, B.M.C., van Meerveld, H.J.L., and Seibert, J. (2017). *J. Hydrol.* 547: 755–769.
- 46 Kirchner, J.W. (2003). *Hydrol. Process.* 17: 871–874.
- 47 Ladouche, B., Probst, A., Viville, D. et al. (2001). *J. Hydrol.* 242: 255–274.
- 48 McGlynn, B.L. and McDonnell, J.J. (2003). *Water Resour. Res.* 39 (11): 1310. doi: 10.1029/2003WR002091.
- 49 Schulte, P., van Geldern, R., Freitag, H. et al. (2011). *Earth Sci. Rev.* 109: 20–31.
- 50 Marc, V., Didon-Lescot, J.-F., and Michael, C. (2001). *J. Hydrol.* 247: 215–229.
- 51 Winston, W.E. and Criss, R.E. (2003). *Environ. Geol.* 43: 546–556.
- 52 Stichler, W., Maloszewski, P., Bertleff, B., and Watzel, R. (2008). *J. Hydrol.* 362: 220–233. doi: 10.1016/j.jhydrol.2008.08.024.
- 53 Kármán, K., Maloszewski, P., Deák, J. et al. (2014). *Hydrol. Sci. J.* 59: 1109–1116. doi: 10.1080/02626667.2013.808345.
- 54 Kebede, S., Travi, Y., and Rozanski, K. (2009). *J. Hydrol.* 365: 173–182.
- 55 Burnett, W.C., Aggarwal, P.K., Aureli, A. et al. (2006). *Sci. Total Environ.* 367 (2-3): 498–543.
- 56 Cartwright, I. and Morgenstern, U. (2018). *J. Hydrol.* 563: 13–21.
- 57 Tweed, S., Munksgaard, N., Marc, V. et al. (2016). *Hydrol. Process.* 30 (4): 648–660.
- 58 Von Freyberg, J., Studer, B., and Kirchner, J.W. (2017). *Hydrol. Earth Syst. Sci.* 21: 1721–1739.
- 59 Bayari, C.S., Ozyurt, N.N., Oztan, M. et al. (2011). *Hydrogeol. J.* 19 (2): 399–414.
- 60 Ma, J.Z., Wang, X.S., and Edmunds, W.M. (2005). *J. Arid Environ.* 61: 277–295.
- 61 Herczeg, A.L. (2001). In: *Water–Rock Interaction* (ed. R. Cidu), 529–532. Rotterdam: Balkema.
- 62 Weyhenmeyer, C.E., Burns, S.J., Waber, H.N. et al. (2002). *Water Resour. Res.* 38 (10): 1184. doi: 10.1029/2000WR000149.
- 63 Druhan, J.L., Hogan, J.F., Eastoe, C.J. et al. (2008). *Hydrogeol. J.* 16: 281–296.
- 64 Dogramaci, S.S. and Herczeg, A.L. (2002). *J. Hydrol.* 262: 50–67.
- 65 Cartwright, I. and Weaver, T.R. (2005). *Hydrogeol. J.* 13 (5 June): 752–770.
- 66 Cartwright, I., Weaver, T.R., Cendón, D.I. et al. (2012). *Appl. Geochem.* 27: 1698–1709. doi: 10.1016/j.apgeochem.2012.02.006.
- 67 Fontes, J. and Ch. and Matray J. M. (1993). *Chem. Geol.* 109 (1–4): 149–175.
- 68 Dutkiewicz, A., Herczeg, A.L., and Dighton, J.C. (2000). *Chem. Geol.* 165: 309–329.
- 69 Cartwright, I., Weaver, T.R., Stone, D., and Reid, M. (2007). *J. Hydrol.* 332: 69–92.